On the Dramatic Importance of Xanthate Substituents in the MADIX Process

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The structural effect of miscellaneous xanthates RS(C=S)OZ' on the level of control of free radical polymerizations was investigated. Such polymerizations referred as to the MADIX process involve the use of xanthates as reversible chain transfer agents (CTAs). In the case of *S*-alkyl-*O*-ethyl xanthates, RS(C=S)OEt, the process involves slow degenerative transfer of xanthate end-groups between polymer chains. This leads to styrene and acrylate-derived polymers with predetermined molar masses at high conversion and polydispersity index (PDI) between 1.5 and 2. In this series, the more substituted and stabilized the R leaving group, the better the control over molar masses as a function of the monomer conversion. Excellent control can be achieved in the polymerization of vinyl esters, acrylic acid and acrylamide.

The reactivity of the C=S double bond of xanthates can be dramatically increased towards polystyryl and polyacrylyl radicals by incorporating electron-withdrawing substituents in the activating Z=OZ' group of *S*-(1-ethoxycarbonyl)ethylenyl-*O*-alkyl xanthates, $C_2H_5OCO(CH_3)CH\text{-}S(C{=}S)OZ'$. This allows the preparation of polymers with controlled molar masses and PDI close to unity.

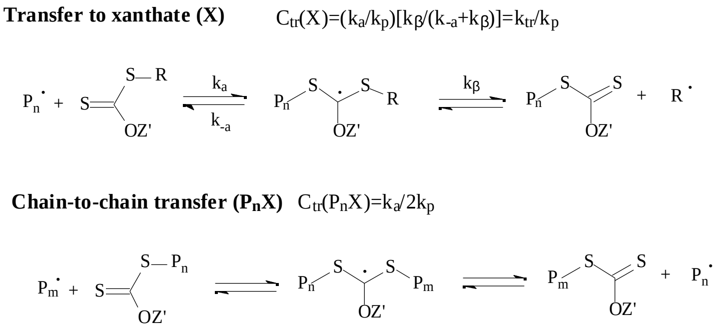
An important development in the area of controlled/living radical polymerization is based on the use of thiocarbonyl thio compounds, Z-C(=S)SR, such as dithioesters, dithiocarbamates, trithiocarbonates or xanthates as reversible chain transfer agents (CTA) in two independently discovered processes. These have been designated Reversible Addition Fragmentation Chain Transfer (the RAFT process) (*1*) and Macromolecular Design *via* Interchange of Xanthates (the MADIX process) (*2*). Both MADIX and RAFT follow a reaction mechanism that was reported in 1988 for the formation of 1:1 adducts (3). Although at the time such radical additions were performed with the more readily accessible xanthates, their obvious extension to other related classes was noted. Theaddition reaction is most simply accomplished by heating an *O*-ethyl xanthate RS(C=S)OEt and an alkene in the presence of a peroxide as initiator. Of particular interest in such a process is the great variety of functional groups and complex substrates which are tolerated (*4*).

The concept of xanthate group transfer radical addition has been successfully extrapolated by the Rhodia group to a new C/LRP system (*2*,*5*). At that time, the discovery of the RAFT process by the CSIRO with dithioesters as controlling agents was still kept under secret (*1*,*6*) and the acronym *MADIX* was proposed for this new fashion of controlling free radical polymerizations involving xanthates. Since then, significant developments have been directed towards RAFT and MADIX processes, including the use of new CTAs such as dithiocarbamates (*7*,*8*) or trithiocarbonates (*9*), kinetical and mechanistic investigations (*1*,*10-15*), direct synthesis of water-soluble materials (*16-19*), or applications of RAFT and MADIX to dispersed media (*1*-2,*20-21*).

On a mechanistic viewpoint, the MADIX and RAFT processes are thus strictly identical and eventually only differ by the nature of the CTA: the RAFT terminology prevails for CTAs Z-C(=S)-S-R in general whereas MADIX refers to xanthates exclusively (with Z = OZ', see Scheme 1) (*1*,*2*).

A fast equilibration relative to the rate of propagation is needed for an optimal control of the polymerization. This can be achieved through variation of the Z and/or the R groups which dramatically affect the chain transfer constant ($C_{tr} = k_{tr}/k_p$) (*1*).

In this contribution, we wish to demonstrate how both R and Z = OZ' groups of xanthates can be finely tuned to reach optimal control of the polymerization. Miscellaneous xanthates have thus been designed and tested in the radical polymerization of various monomers.



Scheme 1. Mechanism of the MADIX process

Experimental

Materials. Monomers were distilled over CaH_2 under vacuum prior to use. The synthesis of **X_1**, **X_2**, **X_4**, and **X_6** to **X_{10}** is described in ref. *2* and *15*. Xanthates **X_3** and **X_5** were synthesized following a procedure similar to that employed for **X_4**, except that 4-cyanobenzaldehyde and 4-methoxybenzaldehyde were used as starting materials, respectively. Xanthates **X_{11}, X_{12}, X_{14}, X_{15} and X_{16}** were.prepared by essentially the same procedure to that detailed below for xanthate **X_{17}**.

Synthesis of xanthate X_{17}.

A 75% aqueous solution of fluoral hydrate (10.0g, 64.6 mmol) and diethylphosphite (64.6 mmol) in triethylamine (9.0 mL, 64.6 mmol) was stirred at room temperature for 15 hrs. The mixture was concentrated and the residue was purified by chromatography (petroleum ether /acétone 10 : 1 then ether, then ether/methanol 10 :1) to give diethyl 2,2,2-trifluoro-1-hydroxy-ethylphosphonate in 82% yield. To an ice-cooled solution of this alcohol (1.44g; 6.1 mmol) in DMF (12 mL) was added carbon disulfide (1.5 ml; 24.4 mmol) followed by the portion-wise addition of sodium hydride as a 60% suspension in oil (244 mg; 6.1 mmol). Stirring was continued for a further 15 minutes and ethyl 2-bromopropionate (0.87 ml; 6.7 mmol) was added, and the resulting mixture was stirred for one hour at 0°C then one hour at room temperature. The red-colored solution was poured into a 1:1 mixture of ether and a saturated aqueous solution of ammonium chloride (200 ml). The organic layer was separated and the aqueous layer further extracted with ether (2 x 200 ml). The combined organic phases were dried over magnesium sulfate and concentrated under vacuum. Purification by chromatography over silica gel (ethyl acetate: petroleum ether 1:4) afforded the desired xanthate **X_{17}** as a 1:1 mixture of two diastereoisomers (690 mg; 58%). ^{1}*H NMR* ($CDCl_3$) δ 4.03-4.37 (m, 7H), 1.75

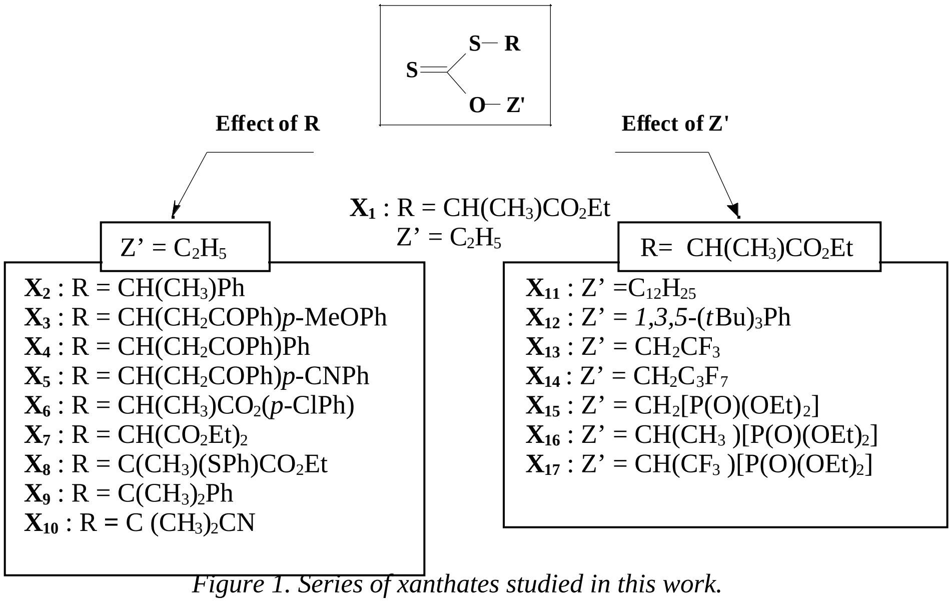
(d, J=6.8 Hz, 3H), 1.20-1.56 (m, 9H) ;^{13}C*MR* (50 MHz, $CDCl_3$) δ 198.0, 170.3, 64.8, 64.7, 61.9, 40.2, 28.4, 15.9, 15.8, 13.8.

***Polymerizations*.** All polymerizations were carried out in sealed tubes after degassing by three pump-freeze-thaw cycles. Transfer constants (C_{tr}) were determined using the Mayo method (conversion < 5 %). Conversion was determined by gravimetry.

***Characterization*.** Molar masses and polydispersities were measured by size exclusion chromatography, using Phenogel columns: Guard, linear, 1000 Å and 100 Å (eluent: THF (1 mL.mn^{-1}). M_n values were calculated based on PS standards.

Results and Discussion

Xanthates can be synthesized from well established organic synthetic routes (*3,4*). Some of the *O*-alkyl xanthates described here (Figure 1) are entirely new compounds and have been purposely designed for this work.



$\mathbf{X_1}$: R = $CH(CH_3)CO_2Et$
Z' = C_2H_5

Z' = C_2H_5
$\mathbf{X_2}$: R = $CH(CH_3)Ph$
$\mathbf{X_3}$: R = $CH(CH_2COPh)$*p*-MeOPh
$\mathbf{X_4}$: R = $CH(CH_2COPh)Ph$
$\mathbf{X_5}$: R = $CH(CH_2COPh)$*p*-CNPh
$\mathbf{X_6}$: R = $CH(CH_3)CO_2$(*p*-ClPh)
$\mathbf{X_7}$: R = $CH(CO_2Et)_2$
$\mathbf{X_8}$: R = $C(CH_3)(SPh)CO_2Et$
$\mathbf{X_9}$: R = $C(CH_3)_2Ph$
$\mathbf{X_{10}}$: R = $C(CH_3)_2CN$

R= $CH(CH_3)CO_2Et$
$\mathbf{X_{11}}$: Z' =$C_{12}H_{25}$
$\mathbf{X_{12}}$: Z' = *1,3,5*-(*t*Bu)$_3$Ph
$\mathbf{X_{13}}$: Z' = CH_2CF_3
$\mathbf{X_{14}}$: Z' = $CH_2C_3F_7$
$\mathbf{X_{15}}$: Z' = $CH_2[P(O)(OEt)_2]$
$\mathbf{X_{16}}$: Z' = $CH(CH_3)[P(O)(OEt)_2]$
$\mathbf{X_{17}}$: Z' = $CH(CF_3)[P(O)(OEt)_2]$

Figure 1. Series of xanthates studied in this work.

Structural Effect of MADIX Agents Z'OC(=S)SR

The effect of xanthates containing the same Z = OEt activating group ($\mathbf{X_1}$ to $\mathbf{X_{10}}$) was first investigated for the polymerization of styrene and ethyl acrylate. These results are summarized in Tables 1 to 3 and Figure 1; complementary data can be found in ref. *15*. In this first series of experiments, it is assumed that the rate constant of addition k_a (Scheme 1) is mainly influenced by the Z = OEt group. Therefore, the results obtained are directly related to the leaving R group ability of these xanthates, that is to the probability ($k_{\beta}/(k_{-a}+k_{\beta})$) for the transient radical to undergo a β-scission (fragmentation step). At low monomer and xanthate conversion, the transfer constant to xanthate, $C_{tr}(\mathbf{X})$, is calculated by the Mayo equation (*1*,*15*)

$$(DP_n)_0=[M]_0/(C_{tr}(\mathbf{X})*[\mathbf{X}]_0) \qquad (1)$$

where $[M]_0$ and $[\mathbf{X}]_0$ are the initial concentration of monomer and xanthate respectively. Before the entire consumption of X, $DP_n > \Delta[M]_t/[\mathbf{X}]_0$. Consequently, a non linear evolution of molar masses (M_n) with monomer conversion is observed, though experimental M_n values eventually match the theoretical ones at high conversion. In other words, the higher the transfer constant, the closer the M_n vs monomer conversion profile to the theoretical straight line which corresponds to an instantaneous xanthate consumption. Generally speaking, these features apply for “living polymerization processes exhibiting slow equilibria” (*22*,*23*). In these polymerizations also, the polydispersity index (PDI) of the polymers is generally much higher than unity (PDI around 2) (*22*).

The R group of *O*-ethyl xanthates has a marked influence on the M_n evolution profile due to a change of the C_{tr} value (see Tables 1 and 2). For instance, the M_n value obtained at high conversion with $\mathbf{X_1}$ is slightly higher than that predicted by [Styrene]/[$\mathbf{X_1}$] feed ratio. This is ascribed to a slow and incomplete consumption of $\mathbf{X_1}$ over the course of the polymerization. This is supported by the C_{tr} value of $\mathbf{X_1}$ lower than unity ($C_{tr}(\mathbf{X_1}) = 0.89$). The chain transfer activity increases in the following order: $\mathbf{X_1} \sim \mathbf{X_2} < \mathbf{X_3} < \mathbf{X_4} \sim \mathbf{X_6} < \mathbf{X_5} \sim \mathbf{X_7} < \mathbf{X_8} < \mathbf{X_9} < \mathbf{X_{10}}$. It turns out that incorporation of electron-withdrawing groups increases xanthate reactivity: $C_{tr}(\mathbf{X_6}) = 1.65 > C_{tr}(\mathbf{X_2}) = 0.82$ and $C_{tr}(\mathbf{X_7}) = 2 > C_{tr}(\mathbf{X_1}) = 0.89$. Also, variation of the electron density of the 1,3-diphenyl-3-oxo-propyl group has a slight effect on the C_{tr}. Indeed, the cyano group of $\mathbf{X_5}$ increases the reactivity as opposed to the methoxy group of $\mathbf{X_3}$: $C_{tr}(\mathbf{X_5}) = 2 > C_{tr}(\mathbf{X_4}) = 1.65 > C_{tr}(\mathbf{X_3}) = 1$. Finally, *O*-ethyl xanthates with tertiary leaving groups further improve the control, the cyanoisopropyl group of $\mathbf{X_{10}}$ proving the best leaving group in this series: $C_{tr}(\mathbf{X_8}) = 3 < C_{tr}(\mathbf{X_9}) = 3.8 < C_{tr}(\mathbf{X_{10}}) = 6.8$. These results are consistent with the findings for dithioesters employed in the RAFT process: the more substituted and stabilized the R° leaving group, the higher the transfer constant (*1*).

Noteworthy, an excellent correlation between the experimental M_n evolution profiles and those predicted by Eq (1) is observed with $\mathbf{X_1}$ to $\mathbf{X_{10}}$, taking into account the C_{tr} values determined by the Mayo method (*15*).

Table 1. Polymerization of Styrene in the Presence of Xanthates.
$[St]_0/[X]_0$=80. T=110 °C.[a]

Entry	*X*	*t (h)*	$M_{n\ th}$[b]	M_n[c]	M_w/M_n	*Conversion*[d] *(%)*
1	**X_1**	2	1050	8000	2.03	10.2
2	**X_1**	90	6550	8150	2.01	76.3
3	**X_3**	0.5	630	8100	2.04	3.2
4	**X_4**	0.5	650	6050	2.06	3.8
5	**X_5**	0.5	530	4650	2.07	2.1
6	**X_{10}**	1	1050	1700	1.85	10.2
7	**X_{10}**	48	7600	7600	2.41	88.9
8	**X_{13}**	2	900	2650	1.93	7.8
9	**X_{13}**	90	5750	5600	1.57	65.8
10	**X_{15}**	1	1150	5250	1.98	9.8
11	**X_{15}**	24	6750	6850	1.90	77
12	**X_{16}**	1	950	6500	2.05	7.2
13	**X_{17}**	5	900	1100	1.10	7.4
14	**X_{17}**	116	6100	6200	1.15	73.7

[a] Entries 1 to 7: Bulk polymerization. Entries 8 to 14: Polymerizations in 50% toluene.

[b] $M_{n\ th}=([M]_0/[Xanthate]_0)*(\text{monomer conversion})*(M_W)_{Monomer} + M_W$ of the xanthate (assuming a complete consumption of **X** and a negligible contribution of the initiator-derived chains).

[c] measured by SEC in THF. Molar masses measurements were based on PS standards.

[d] conversion was determined gravimetrically.

Table 2. Polymerization of Ethyl Acrylate (EA) in the Presence of Xanthates. $[EA]_0$=4.6 M, $[X]_0$=5.75 .10^{-2}M, $[AIBN]_0$=1.72.10^{-3} M. T=80 ^oC. Solvent: Toluene.

Entry	*X*	*t (h)*	$M_{n\ th}$ [a]	M_n [b]	M_w/M_n	*Conversion*[c] *(%)*
1	$\mathbf{X_1}$	0.17	1150	5700	1.81	11.6
2	$\mathbf{X_1}$	3.5	7940	7290	1.77	96.5
3	$\mathbf{X_9}$	1	2160	1990	2.11	24
4	$\mathbf{X_9}$	5.5	8200	7500	1.57	98.8
5	$\mathbf{X_{10}}$	0.5	1100	1400	2.05	11.4
6	$\mathbf{X_{10}}$	4	7320	8100	1.53	89.1
7	$\mathbf{X_{11}}$	0.4	1450	5640	1.76	13.7
8	$\mathbf{X_{11}}$	2	7760	7320	1.73	92.5
9	$\mathbf{X_{12}}$	1.5	4530	60500	1.63	51
10	$\mathbf{X_{13}}$	0.33	1150	2950	1.90	11.0
11	$\mathbf{X_{13}}$	2.33	7650	7950	1.42	91.8
12	$\mathbf{X_{14}}$	1.5	8400	7100	1.41	81.8
13	$\mathbf{X_{17}}$	0.25	1100	900	1.26	8.6
14	$\mathbf{X_{17}}$	0.42	4400	4400	1.12	49.6
15	$\mathbf{X_{17}}$	1	7000	6900	1.14	82.6

[a] $M_{n\ th}=([M]_0/[Xanthate]_0)*$ (monomer conversion)* $(M_W)_{Monomer}+ M_W$ of the xanthate (assuming a complete consumption of X and a negligible contribution of the initiator-derived chains)

[b] measured by GPC in THF. Molar mass measurements were based on PS standards.

[c] conversion was determined gravimetrically

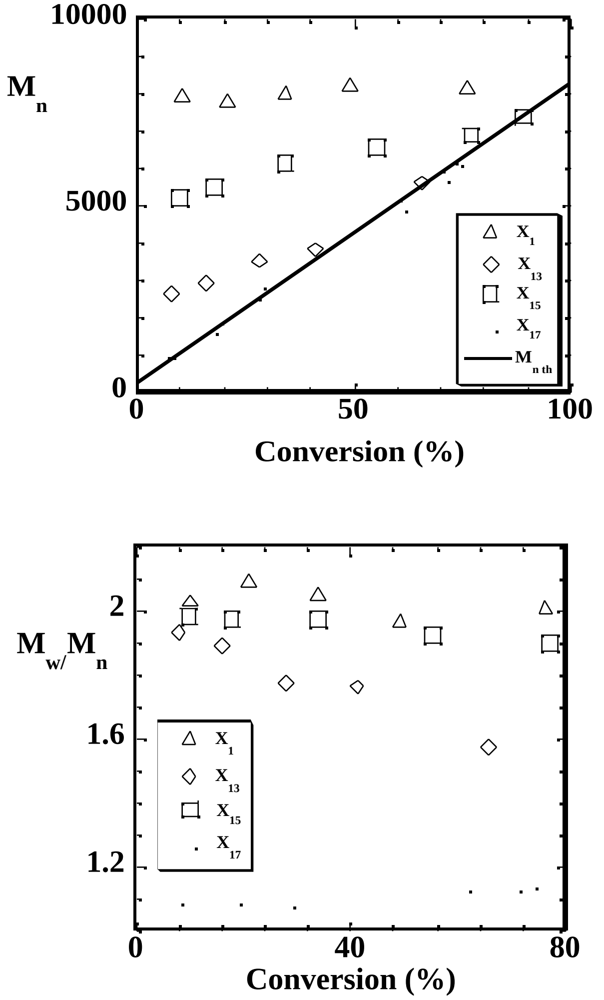
On the other hand, little influence of the R group on the molar mass distributions is observed: PDIs are typical of those obtained in a xanthate-free polymerization (1.9-2.4). This is ascribed to a slow interchange of the xanthate end-groups between polymer chains, that is to a low $C_{tr}(\mathbf{P_nX})$. Catala and coll. (*24*) have recently calculated the chain transfer constant value of a *S*-polystyryl-*O*-ethyl xanthate and found $C_{tr}(\mathbf{P_nX}) = 0.8$, that is a very close value to $C_{tr}(\mathbf{X_2})$ which is equal to 0.82 (*15*). This verifies, in this particular case, that the phenylethyl group exhibits the same leaving ability as the polystyryl chains. The observation of PDIs around 2 are consistent with the statement by Müller and coll. who have predicted that the PDI of “living” polymerization involving slow equilibria evolves according to the following formula (*22*).

$$PDI = 1 + 1/C_{tr}(P_nX) \qquad (2)$$

Despite the rather high PDI values, excellent control of chain structures is achieved, as evidenced by NMR analysis and MALDI-TOF mass spectroscopy (*15*): no chains derived from thermally generated radicals have been detected. This high “end group fidelity” eventually allowed block copolymer synthesis from xanthate-capped homopolymers serving as macro-CTA in chain extension experiments (*2*,*5*).

Importantly, the nature of the R group has no significant influence on the overall rate of polymerization for this series of xanthates. Significant retardation is only observed with $\mathbf{X}_{9}$, presumably due to degradative transfer (*15*).

Next, the effect of the activating group Z = OZ’ of the xanthates on the quality of control of MADIX was investigated. This was achieved using a series of xanthates carrying the same R leaving group, namely a (1-ethoxycarbonyl)ethyl group. Both electron density and steric hindrance of the Z = OZ’ group were varied. In this case, the differences observed can be related to a difference of reactivity of the C=S double bond towards growing radicals. The results are summarized in Tables 1 and 2 and Figure 2. First of all, one can note that there is no influence of *O*-alkyl chain length on the quality of control, $\mathbf{X}_{1}$ and $\mathbf{X}_{11}$ giving roughly the same results. Introduction of a bulky group such as tris-(*tert*-butylphenyl) group in α-position to the oxygen prevents the growing radicals from accessing the C=S double bond of xanthate $\mathbf{X}_{12}$, which proves ineffective as MADIX agent. For MADIX polymerization of styrene and ethyl acrylate, the chain transfer activity decreases in the following order: $\mathbf{X}_{17} > \mathbf{X}_{13} \sim \mathbf{X}_{14} > \mathbf{X}_{15} > \mathbf{X}_{1} \sim \mathbf{X}_{11} > \mathbf{X}_{16} \gg \mathbf{X}_{12}$. It appears that the perfluoroalkyl chain length has no influence on the activity of xanthates, $\mathbf{X}_{13}$ and $\mathbf{X}_{14}$ giving similar results. As for $\mathbf{X}_{17}$, it is fully consumed before 10% of the monomer is converted, resulting in a linear increase of the molar masses as a function of monomer conversion from the early stages of the polymerization, with Mn values perfectly matching the theoretical ones based on the [styrene]/[$\mathbf{X}_{11}$] ratio.



2a.

2b.

Figure 2. Evolution of (2a) M_n and (2b) M_w/M_n during polymerization of styrene in the presence of xanthates with various Z' groups. $[M]_0/[X]_0=80$. Thermal polymerization at 110°C, in 50% toluene.

Figure 2b shows that the *O*-alkyl group has also a dramatic impact on PDIs. The moderate reactivity of *O*-ethyl xanthates is attributed to the conjugation of the lone pairs of electrons on the oxygen atom with the C=S bond, resulting in low k_a values (*1,2*). It is interesting to note in this respect that dithiocarbamates with no electron-withdrawing groups on the nitrogen atom are poor transfer agent since conjugation with the electron pair on the nitrogen has an even greater stabilizing effect on the thiocarbonyl group. However, in the case of xanthates, the enhanced capability for transfer (increase of both $C_{tr}(\mathbf{X})$ and $C_{tr}(\mathbf{P_nX})$- Scheme 1) leading to a significant decrease in the PDI is achieved through the use of a fluoro-alkyl substituents in the Z' moiety. This can be rationalized by the fact that the conjugation effect mentioned above is considerably reduced with such electron-withdrawing substituents.

Of particular interest, the 1-diethoxyphosphonyl and 2,2',2''-trifluoromethyl groups on the α-carbon bonded to the oxygen atom have a cooperative effect since $\mathbf{X_{17}}$ further activates the chain transfer process, as compared to $\mathbf{X_{13}}$ and $\mathbf{X_{14}}$. It appears, however, that the introduction of the diethoxyphosphonyl group alone is not sufficient to enhance the reactivity of these xanthates since the substitution of the CF_3 group for a methyl group ($\mathbf{X_{16}}$) or a hydrogen ($\mathbf{X_{15}}$) results in a moderate control. The fact that $\mathbf{X_{15}}$ is slightly better than $\mathbf{X_{16}}$ is explained by the donating inductive effect of the methyl group which stabilizes the C=S double bond.

The scope of the MADIX process

As emphasized above, xanthates afford variable control over PDIs and molar masses depending on their substituents as well as on the monomer undergoing polymerization. In other words, there is no MADIX agent (neither RAFT agent) that would exhibit a universal character. It appears that the higher the reactivity of the propagating radicals (e.g. those deriving from vinyl acetate), the better the control of the polymerization with *O*-ethyl xanthates. In contrast, the reactivity of these MADIX agents is moderate towards polystyryl radicals, slightly improved with polyacrylyl radicals and they are ineffective towards poorly reactive radicals such as polymethacrylyls (*1-2,15*).

Case of Alkyl Acrylates

Polyacrylyl-based radicals exhibit relatively low steric hindrance and are highly reactive. With properly selected xanthates efficient control of the polymerization of acrylates is achieved. For instance, *O*-ethyl xanthates are mildly effective towards acrylates, although they can provide excellent control over molar masses vs monomer conversion profiles, in particular with a tertiary R leaving group. This is illustrated in the Figure 3 below. Also, *O*-ethyl xanthates produce polyacrylates with lower PDIs (entries 1 to 6 in Table 2) as compared to polystyrene samples (Table 1), suggesting more rapid interchange of the dithiocarbonate moieties -higher $C_{tr}(\mathbf{P_nX})$- during polymerization of acrylates, as compared to styrene polymerization. As discussed above, however, control is highly improved by fine tuning the Z = OZ' of xanthates (entries 7 to 15 in Table 2).

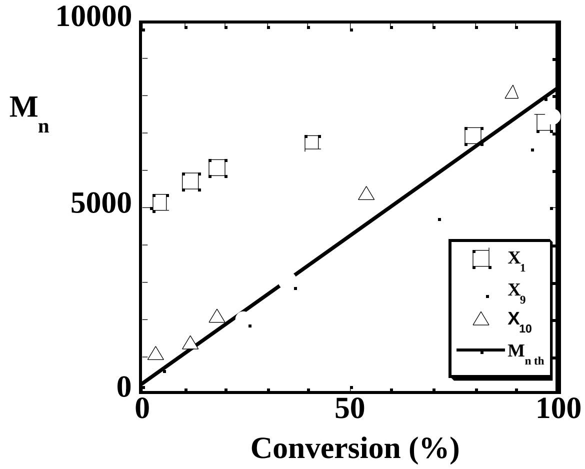


Figure 3. Mn vs conversion in MADIX polymerization of EA in the presence of O-ethyl xanthates with different leaving groups. Conditions of Table 2.

Case of Vinyl Esters

Whereas the polymerization of vinyl esters has been shown to be completely inhibited in the presence of dithioesters as RAFT agents, excellent control over molar masses and PDIs is achieved with a MADIX agent such as $\mathbf{X_1}$ in the polymerization of vinyl acetate, vinyl neodecanoate and vinyl stearate (Table 3). In such cases, $\mathbf{X_1}$ is entirely consumed in the early stage of the polymerization resulting in a linear increase of the molar masses with conversion of the monomer. The MALDI TOF mass spectrum of a poly(vinyl acetate) sample prepared with $\mathbf{X_1}$ shows the perfect agreement of the chain structure with the expected one (Figure 4). As already reported (*1,2,7,8*), the fact that xanthates (or particular dithiocarbamates as RAFT agents) are agents of choice for controlling the polymerization of vinyl acetate is explained by the stability of the intermediate radical (scheme 1). The latter species may undergo a β-scission much faster than when a dithioester is employed as a RAFT agent. Indeed, a stable xanthate-capped polymer chain is produced after fragmentation due to the conjugation effect mentioned above.

Table 3. Polymerization of Vinyl Esters in the Presence of X_1.

Entry	*M*	*[AIBN]$_0$/[$\mathbf{X_1}$]$_0$/[M]$_0$*	*t (h)*	$M_{n\ th}$	M_n[a]	M_w/M_n	*Conv (%)*
1	**VOAc**[b]	0.03/1/80	2.66	1750	1400	1.32	22.3
2	**VOAc**[b]	0.03/1/80	8	1100	1300	1.21	60.3
3	**VneD**[c]	0.15/1/10	3	2000	1600	1.12	90
4	**VneD**[c]	0.15/1/30	3	5300	4550	1.22	86
5	**Vste**[d]	0.15/1/10	21	3250	3750	1.18	93
6	**Vste**[d]	0.15/1/40	21	11250	10500	1.31	85

[a] measured by SEC in THF. Molar mass measurements were based on PS standards.

[b] Polymerizations of vinyl acetate performed in bulk, at 60 °C.

[c] Polymerization of vinyl decanoate performed in bulk, at 70 °C.

[d] Polymerization of vinyl stearate performed in 50% solution (ethyl acetate/cyclohexane=30/70), at 70 °C.

[e] Polymerization of vinyl stearate performed in a 70% cyclohexane solution, at 70°C.

Figure 4. MALDI-TOF mass spectrum of a PVOAc-X_1 sample (entry 3, table 3).

Case of hydrophilic monomers: Acrylic Acid and Acrylamide

The controlled nature of MADIX is preserved when applied to functional monomers such as acrylic acid and acrylamide without resorting to protective groups (*16,19*). Radicals deriving from these two monomers have little streric bulk and are highly reactive. Therefore, xanthates are well-suited to control the polymerization of these monomers. Mono- and difunctional xantathes have been successfully used in the sequential polymerization of acrylic acid and acrylamide in aqueous medium. Double hydrophilic statistical, diblock and triblock copolymers made of polyacrylamide and poly(acrylic acid) have been synthesized in this way (*19*).

Conclusion

The MADIX technology relies on the interchange of dithiocarbonate groups at the polymer chain ends providing control for free radical polymerizations of miscellaneous monomers, including styrenics, acrylics and vinyl esters. The design of the xanthate CTA is crucial for an optimal control of molar masses evolution and polydispersity. In *O*-ethyl xanthates, the R leaving group only affects the first transfer event, that is the chain transfer constant to the xanthate, $C_{tr}(X)$. Xanthate reactivity is optimal with tertiary leaving groups like the cyanoisopropyl group. The polydispersity is dictated by the chain transfer constant to the $P_nS(C{=}S)OEt$ chain end, like in any "living" process involving slow equilibria. The moderate reactivity of *O*-ethyl xanthates is related to the conjugation between the oxygen atom of the *O*-ethyl group and the C=S double bond. However, dramatic increase of the reactivity of xanthates is achieved through the incorporation of electron-withdrawing groups in the β-position to the oxygen atom, minimizing the conjugation effect and resulting in much narrower distributions of molar masses and structurally well-defined materials.

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